

Proceedings of the American Academy of Arts and Sciences.

VOL. XXXV. No. 18. — MARCH, 1900.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY
OF HARVARD COLLEGE.

*ON THE DETERMINATION OF SULPHURIC ACID IN
THE PRESENCE OF IRON; A NOTE
ON SOLID SOLUTIONS.*

BY THEODORE WILLIAM RICHARDS.

THE UNIVERSITY OF CHICAGO

THE DIVISION OF THE PHYSICAL SCIENCES

DEPARTMENT OF CHEMISTRY

CHICAGO, ILL.

1911

REPORT OF THE DIVISION OF THE PHYSICAL SCIENCES

FOR THE YEAR 1911

CHICAGO, ILL.

THE UNIVERSITY OF CHICAGO

THE DIVISION OF THE PHYSICAL SCIENCES

DEPARTMENT OF CHEMISTRY

CHICAGO, ILL.

1911

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY
OF HARVARD COLLEGE.

ON THE DETERMINATION OF SULPHURIC ACID IN
THE PRESENCE OF IRON; A NOTE
UPON SOLID SOLUTIONS.

BY THEODORE WILLIAM RICHARDS.

Received February 5, 1900. Presented February 14, 1900.

WITHIN the past year have appeared three interesting articles by Küster and Thiel* concerning several methods of precipitating baric sulphate free from iron when that element has been present in the solution. One of the methods which they have proposed is an excellent addition to our always imperfect analytical repertory, and the chemical world owes them a debt for the ingenious although exceedingly simple suggestion.

While not wishing in the least to detract from the merit and interest of this work, I feel that attention should be called to several omissions in their paper, especially those which concern theoretical considerations involved in previous work upon the subject.

In their first paper, where the admirable analytical device is explained, Küster and Thiel ascribe the "occlusion" of iron to the presence of the ferric ion. It is interesting that this idea, which they themselves have since shown to be false, should have led them to the desired goal. The circumstance might be taken as an argument in favor of the proposition that even an incorrect idea is better than none. In a reference to this paper, Ostwald† points out that the occlusion is in all probability due not to the ferric ion, but rather to a molecular complex; and in their last paper Küster and Thiel describe experiments which prove beyond much doubt the correctness of Ostwald's suggestion. Oddly enough, however, they still cling, in their summing up of the matter, to the statement that the ferric ion is the essential agent.

* Küster and Thiel, *Z. anorg. Chem.*, **19**, 97 (1899); **21**, 73 (1899); **22**, 424 (1900).

† Ostwald, *Z. phys. Chem.*, **29**, 340 (1899).

It is curious also that they should have overlooked the following statement in a paper published over ten years ago by Professor Jannasch and myself. In speaking of the cause of the phenomenon under consideration, we said: "Es lässt sich unmittelbar annehmen, dass das Eisen als eine Doppelverbindung mit Baryum als Baryum-Ferrisulphat gefällt wird, welches wahrscheinlich ein Molekül gebundenes Wasser (sogen. Constitutionswasser) enthält."* Küster and Thiel have offered new arguments which they consider as being in favor of the first part of this proposition, without appearing to recognize that the proposition is not itself new. They have moreover ascribed an arbitrary formula to the substance, while we did not feel prepared either to assume its exact nature or to explain the mechanism of its occlusion.

Three years after this publication Schneider described some interesting experiments in which evidence was given that the occlusion of the double or complex compound is a variety of solid solution.† The idea was new at the time, and did not meet with general favor; but a knowledge of the work would have saved Küster and Thiel trouble.

In 1894,‡ after the passing of two more years, Gladding published a modification of Lunge's method of precipitating baric sulphate free from iron, which is the most convenient of any which had appeared up to that time. He precipitated the iron with ammonia, filtered without especial washing, acidified the filtrate, added an excess of baric chloride, and then collected on one filter both the main mass of the baric sulphate and the small amount of the same substance which he obtained from the ferric hydroxide. The chief difference between this method and the method of Küster and Thiel is the fact that the latter pointed out the uselessness of filtering off the ferric hydroxide before adding the baric chloride. It is quite probable, however, that Küster and Thiel did not know of Gladding's work, and hence independently devised the whole process.

Let us consider for a moment the nature and cause of this kind of occlusion. In the first place it must be distinguished sharply from the mechanical retention of mother-liquor in minute cells which all crystalline precipitates exhibit. Even large crystals rarely contain cells of included mother-liquor plentiful enough to increase their weight by more than the fraction of a percent; and this impurity is of course chiefly water. It is easy to test the magnitude of this *inclusion* by precipitating such a substance as calcic carbonate from a solution containing a large quantity of

* Jannasch and Richards, J. prakt. Chem. [2], 39, 321 (1880).

† E. A. Schneider, Zeitschr. phys. Chem., 10, 425 (1892).

‡ T. S. Gladding, Jl. Am. Chem. Soc., 16, 398 (1894); 17, 347 (1897).

some easily identified substance such as sodic chloride. Mr. R. P. Cushing kindly made a number of such experiments for me, and found that not even from a saturated solution of salt did more than 0.1 percent of the precipitate consist of sodic chloride. Of course this value fixes the maximum, for some of the substance may well have been *occluded* instead of *included*.

Very different from the mechanical process of *inclusion* is the behavior of baric sulphate. Here the impurities may amount to several percent, and the foreign material is disseminated equally throughout the mass. The experiments of Schneider show that the amount of the occlusion is greater as the concentration of the impurity in the solution increases, although not in direct proportion. It is very clear that we are dealing here with a special case of the distribution law; but in this case the distribution can take place only at the moment of precipitation, because afterwards the rigidity of the solid prevents free motion. Küster and Thiel evidently thought of this possibility, but they did not amplify the idea. In the present paper I have retained the name occlusion for this phenomenon because no other term seems to be applicable. There is indeed a certain analogy between the occlusion of hydrogen in palladium and the dissemination of a solute out of a solution into a solid; and since the name gives rise to no misunderstanding it will answer its purpose.

Obviously the study of the distribution law in other cases should throw light upon this one by analogy. When hydrochloric acid is distributed between its aqueous solution and the vapor phase, the concentration of the undissociated part alone is concerned in the distribution, because ions can exist only in the solution. In the same way, when a moderately strong acid is distributed between water and ether, only the undissociated part of the acid comes into play, because ether does not cause important dissociation. From these analogies one might infer that the group which is concerned in cases of concomitant precipitation are not ions, but rather electrically neutral complexes. The inference is not a perfectly safe one, for little is known about the possible degree of dissociation in solids; but experimental evidence is at hand to support this view. In 1894 Richards and Parker made the observation that the occlusion of baric chloride by baric sulphate is much increased by the previous addition of hydrochloric acid to the solution of baric chloride.* For example, the addition of twenty cubic centimeters of strong hydrochloric acid caused almost twice as much occlusion as the addition of ten cubic centimeters

* Proc. Am. Acad., 31, 74 (1894); Z. anorg. Chem., 8, 420 (1895).

in another otherwise similar case. The conditions attendant upon mixing two liquids are so uncertain that it is unsafe to attempt the quantitative interpretation of the relationship; but qualitatively this result is wholly in accord with the law of mass action, provided that the undissociated group is supposed to be the one concerned.

The nature of the electrically neutral group with which we have to do in the present case is less easy to imagine. Küster and Thiel assume that it is $\text{Ba}[\text{Fe}(\text{SO}_4)_2]_2$; but this is evidently an unsafe assumption. The analogy to the case of chromium which they quote is an excellent point, but they do not seem to have made themselves conversant with the literature upon this subject, and hence apply their useful analogy unfortunately.

They seem to consider that chromium exists in the green solution as part of an acid ion, instead of in the basic semi-colloidal form ascribed to it upon excellent grounds by both Recoura and Whitney.* One could hardly expect a basic substance to form such a salt as Küster and Thiel's with barium.

Some light upon the subject is to be had from the study of the quantitative results in the paper of Jannasch and myself before mentioned. We found that the impure baric sulphate precipitated from a ferric solution (containing enough sulphuric acid to have yielded 1.1608 grams of pure baric sulphate) as a matter of fact weighed on the average only 1.1170 grams, and contained 0.0144 gram of ferric oxide, hence the baric sulphate actually present amounted to $1.1170 - 0.0144 = 1.1026$ grams. This is 0.0582 gram less than the amount which should have been present; hence, supposing that no sulphuric acid remained in the solution, there must have been $0.0582 \frac{\text{SO}_3}{\text{BaSO}_4} = 0.0199$ gram of sulphur trioxide in the iron complex. But 0.0144 gram of ferric oxide corresponds to 0.0216 gram of sulphur trioxide in ferric sulphate; hence there was a deficiency of nearly two milligrams. If sulphuric acid remained in solution, the deficiency in the complex must have been still greater. It is true that the observed difference is only half so great as that demanded by a formula analogous to Recoura's, $\text{Fe}_4(\text{SO}_4)_6(\text{OH})_2$, and is perhaps not very much greater than a possible experimental error; but, as far as the argument goes, it points toward the existence of a basic complex in the precipitate.

* A convenient résumé of the argument in favor of this point of view is to be found in a recent article by Whitney, *Jl. Am. Chem. Soc.*, **21**, 1075 (1899).

Turning to the results of Küster and Thiel's work, we find other arguments indicating the same thing. On pages 439-440 of their third paper they point out that the addition of acid diminishes very much the occlusion of the iron complex. This is wholly consistent with the present thesis: for (according to the Mass Law) the addition of acid must diminish the concentration of the basic complex in the solution, and hence (according to the distribution law) the amount which finds its way into the solid. It is true that this argument is somewhat diminished in force by two circumstances: first, because Küster and Thiel have not here considered the fact that hydrochloric acid increases the weight of the precipitate by introducing into it more baric chloride; and second, because the addition of hydrochloric acid undoubtedly causes a chloride-complex which is not occluded to nearly so great an extent as the sulphate-complex by the baric sulphate. In order really to study the effect of the hydrogen ion one should not rely simply upon the total weight of the mixed precipitate, but should actually determine the amount of iron present in the precipitate and compare it with the amount present in a precipitate obtained from a solution containing the same amount of iron and an amount of sodic chloride equivalent to the hydrochloric acid used in the first case. In spite of these objections, however, the effect observed by Küster and Thiel is so great that one must ascribe a portion of it to the action of the hydrogen ion, and hence, according to Whitney and Recoura, infer the substance concerned to be a basic complex. Küster and Thiel offered no explanation for the action of the hydrogen ion.

Again, Küster and Thiel point out (pp. 437-438) that the hydrolysis caused by dilution prevents the addition of much water from causing as considerable a decrease in the absorbed material as would otherwise have been expected. This is equivalent to saying that the complex which is concerned is a basic one: for the hydrolysis undoubtedly involves the ionization of hydrogen.

Yet another, although less cogent, argument in favor of the basic nature of the complex is the fact that Jannasch and I found the impure baric sulphate to be capable of retaining about three per cent of water at 250°. While it is not impossible that this should be at least in part simply held in minute cells or as crystal-water, one is inclined to ascribe part of it to hydroxyl existing in the precipitate. It may well be, however, that the extra water is simply dissolved in the precipitate, as other undissociated substances are dissolved by baric sulphate. This tendency to dissolve water may be the reason why

many precipitates require prolonged ignition in order to attain constant weight.

Over a year ago I was attracted by the observation that green chromic sulphate is plentifully occluded by baric sulphate,* into beginning a study of the subject of occlusion with the help of this phenomenon. Chromium was selected instead of iron because its complex is more stable and has been more thoroughly studied. The research was begun by Mr. R. P. Cushing and is being continued by Mr. F. Bonnet. Since the precipitated baric sulphate is green, one must infer immediately that the green modification (or complex) is responsible for the occlusion. The work is not yet ready for publication, but our data agree well with those of Küster and Thiel, while our explanation accords with that given in the present paper. We are also studying aluminum sulphate, which likewise seems to form a complex very considerably occluded by baric sulphate; although this fact does not seem to be generally known.†

This paper is intended to serve as an introduction to two other papers upon specific cases of occlusion. The chief points upon which emphasis is desired are the following:—

(1) *Occlusion* from solutions differs from *inclusion* by being a more intimate and a less mechanical mixture.

(2) Occlusion differs from *adsorption* in concerning the whole mass of the precipitate, and not merely its surface. Hence after a precipitate is once formed occlusion takes place only with extreme slowness, because of the rigidity of solids. New evidence of this will be given in one of the following papers.

(3) Different precipitates have almost as widely varying powers of occluding other substances as different liquids have widely varying powers of dissolving other substances. The property is no more to be predicted than the power of dissolving.

(4) The process of occlusion is probably the distribution of an electrically neutral simple substance or complex between the solution itself and the solid at the moment of its formation within the solution. Hence any change in the substances present in the solution which tends to diminish the concentration in the solution of the group under consideration, tends to diminish the amount occluded.

* This circumstance has been independently observed by Whitney, Jour. Am. Chem. Soc. **21**, 1075 (1899).

† Compare Peckham, Jl. Am. Chem. Soc., **21**, 772 (1899).

(5) The nature of the groups which are occluded in the cases of iron, chromium, and aluminum is not yet determined, but they are probably basic in nature, and identical with the complexes of Recoura and Whitney.

HARVARD UNIVERSITY, CAMBRIDGE, MASS.,
February 2, 1900.